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Effect of hydrogen diffusion on the thermo emf of tantalum zirconium and titanium

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Wires of tantalum, zirconium and titanium metals were subjected to cathodic hydrogen diffusion. Thereafter the changes in the thermo emf were measured as the wires lost hydrogen with time. The so obtained results can be interpreted in terms of the band structure of the metals.

1. INTRODUCTION

An interesting feature of the phenomena of hydrogen diffusion in metals of groups III A to VII A and group VIII is that the unfilled part of the *d*-band gets filled by the electrons donated by the diffused hydrogen The various physical properties of the metal show a temporary change. The hydrogenated metal if left to itself tries to return to its original state. During this period the changes in resistivity and thermo emf reveal the details of the unfilling (or emptying) process of the *d*-band We have studied nickel (Nigam & Garg 1972), iron and cobalt (Nigam & Rani 1975) taken in form of wires after subjecting them to cathodic hydrogen diffusion However, the foils behave differently (Nigam & Rani 1975). The interpretation involves the use of surface states[+]. The present paper describes the thermo emf measurements made on hydrogenated tantalum, zirconium and titanium *wires*, in contrast to the earlier work (Berlincourt & Bickel 1970, Tanaka & Hoshimoto 1973, Bickel & Berlincourt 1970) done with foils.

2. EXPERIMENTAL

Cathodic hydrogen diffusion. Wires having 20 cm length and 0.2 mm diameter were subjected to hydrogen diffusion by being fixed to the platinum cathode in an electrolysis cell. The anode was also a platinum electrode. The electrolyte consisted of a solution prepared by mixing 10 ml of H_2SO_4 and 0.2 g thio urea in one liter of distilled water. The hydrogenated metal is brittle and so the twisted electrical contacts were avoided. The wire to be hydrogenated was hung vertically in the tube shaped cell and carefully taken out after the electrolysis was over. A 6 volt battery served as the source of current which was kept fixed at 30 mA. The electrolysis was carried out for 200 hours.

Measurement of thermo emf. A standardized ten wire potentiometer was used for the thermo emf measurements (Nigam & Garg 1972) Couples were dipped in mercury for good electrical contacts In case of tantalum the couple was made with constantan while in case of zirconium and titanium, copper was used. The formation of amalgam with copper does not occur during the short time in which the experiments are performed If at all any amalgam is formed it does not affect our results within the limits of our errors The cold junction was maintained at the temperature of melting ice while the hot one was kept at the room temperature. First the measurements were done with pure wire as sample. When the devices were set, the electrolysis going in for the past 200 hours was stopped and a stop watch started The hydrogenated wire was fixed in position and the measurements started as described earlier (Nigam & Garg 1972) The variation in thermo emf with time of outgassing was recorded.

3. Results and Discussion

We will discuss the results for each metal separately.

(a) *Tantalum* : According to Nigam & Garg (1972) thermo emf is proportional to the gradient of the density of states curve i.e , to dn/dE. The variation in thermo emf with time as shown in figure 1 represents the variation in dn/dE

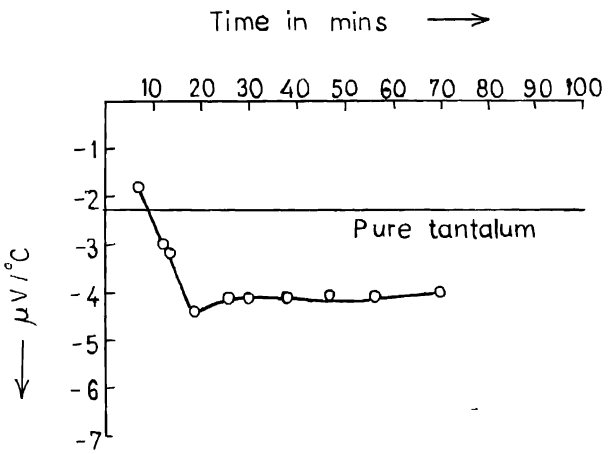

Fig. 1

with time for tantalum. A theoretical calculation of $n(E)$ versus E was made by Petroff & Vishwanathan (1971) who used $5d^3\ 6s^2$ free atom configuration for tantalum to construct the energy bands. These authors have represented their

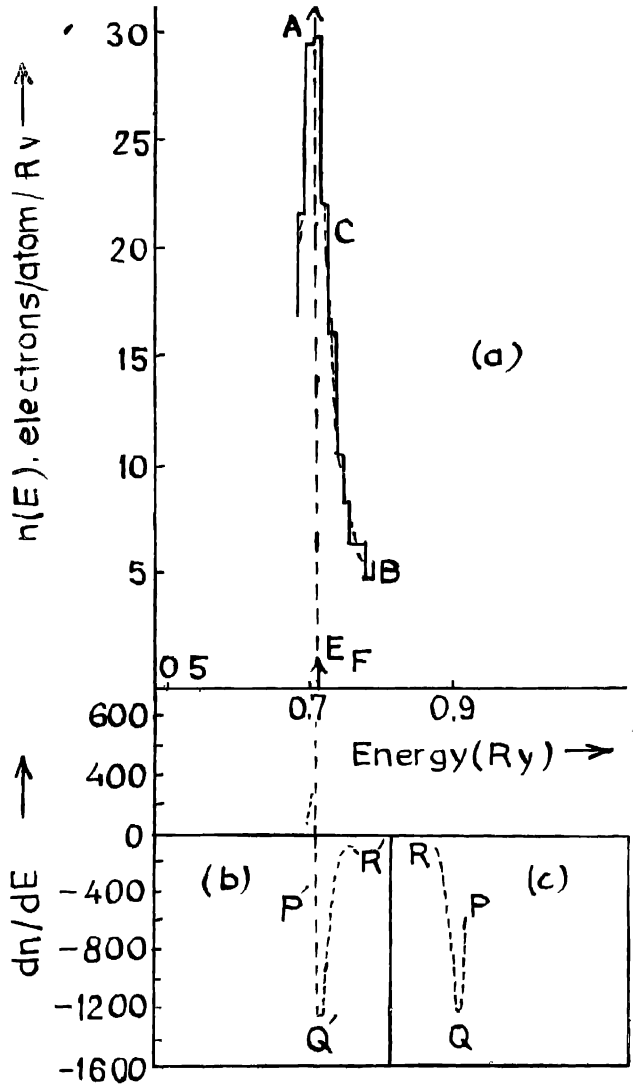
n(E), electrons/atom/Ry
30
25
20
15
10
5
A
C
B
(a)
0 5
E_F
0.7
0.9
Energy(Ry)
600
400
0
dn/dE
-400
-800
-1200
-1600
(b)
P'
R'
Q'
R
P
Q
(c)

Fig. 2

results in form of a histogram. No other calculations on this metal are available. To obtain a crude and tentative estimate we have smoothened out this histogram to get the curve shown in figure 2a. Point A is the position of the Fermi level. This curve was numerically differentiated in the range A–B and the so obtained dn/dE vs E curve is shown in figure 2b. When the band is full due to hydrogenation, the emptying out process will begin from the higher energy side. For this reason the mirror image of figure 2b is drawn in figure 2c. This will be compared with the results shown in figure 1 Only the part PQR of figure 2c is observed in figure 1. The corresponding points in figure 2b are marked as P', Q', R' and in figure 2a as A, C and B We conclude that whereas the filling in process of the band starts from A and continues up to B, the emptying out process does not return up to the point A but stops at C corresponding to the point P in figure 2c. At B the filling in process stops because the value of $n(E)$ is low (Nigam & Rani 1975). The emptying is incomplete due to the formation of the covalent hydride (Libowitz 1965). This is the band interpretation of our results.

Berlincourt & Bickel (1970) and Tanaka & Hoshimoto (1973) diffused hydrogen in thin foils of tantalum and found that the sign of the thermo emf was

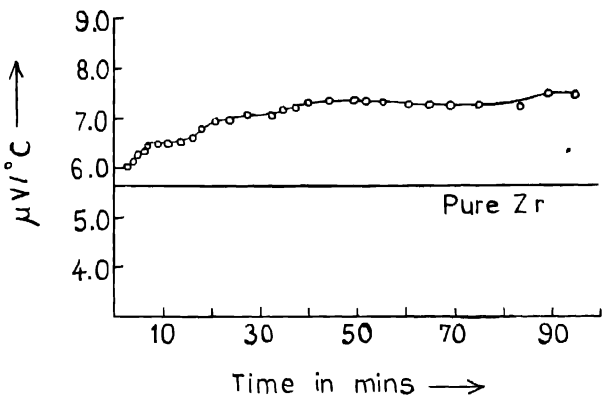

Fig. 3

reversed. This reversal of sign seems to be a property characteristic of the foils. We observed that this happens in case of nickel as well (Nigam & Rani 1975).

(b) *Zirconium* : The results for zirconium metal are shown in figure 3. The changes in thermo emf are rather small. The sign of the Hall constant of zirconium is suggestive of hole conduction (Bickel & Berlincourt 1970). For this reason we have to slightly modify our earlier method of interpretation which

we have successfully applied to nickel (Nigam & Garg 1972), iron and cobalt (Nigam & Rani 1975) and presently to zirconium.

Figure 4a shows that density of states curve for zirconium metal as given by Altmann & Bradley (1968). At the Fermi level the density of states is low

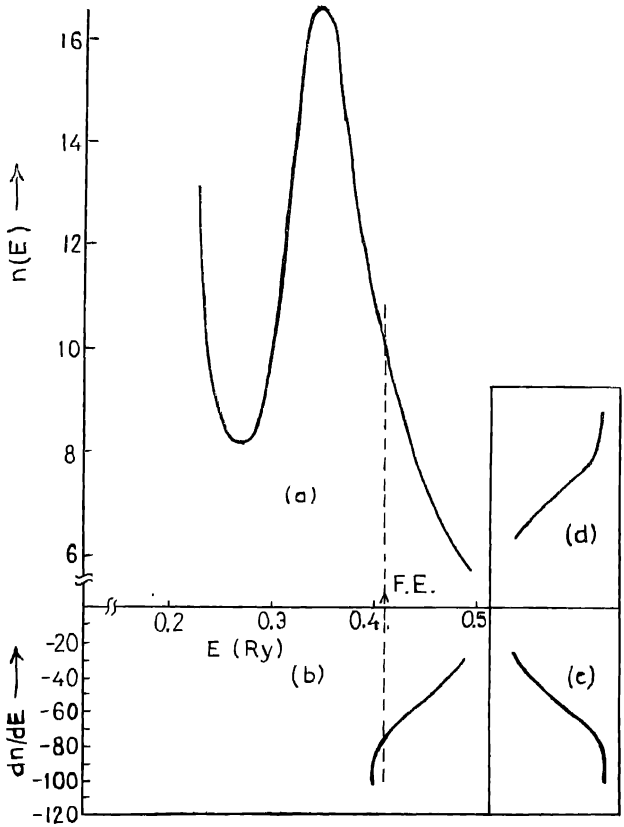

Fig. 4

and so is also the probability of hydrogen diffusion. The variation in thermo emf due to the band filling will also be small. In figure 4b is shown the dn/dE curve obtained by numerical differentiation. The mirror image of figure 4b about the y-axis is drawn in figure 4c. Since the conduction is by holes instead

of electrons we have to reverse the sign of dn/dE in figure 4c. We do so, by, drawing the mirror image of figure 4c about the axis of x in figure 4d, and obtain a curve which resembles our experimental curve shown in figure 3. The thermo emf rises slightly and then becomes constant. Since the earlier work (Bickel & Berlincourt 1970) was done with foils there is no point in comparing the results obtained for wires. In foils the surface states dominate and should be taken into account to explain the electrical properties. We have obtained results indicative of the part played by the surface states*.

(c) *Titanium* : Our results for titanium are very much similar to those for zirconium. This is in conformity with the fact that their density of states curves are also similar. For the sake of brevity we omit the reproduction of these curves and also our results There is one point of interest here Ducastelle *et al* (1970) have mentioned that despite the similarity of the band structures of zirconium and titanium the sign of the Hall coefficient is different The reason for this is still not known.

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